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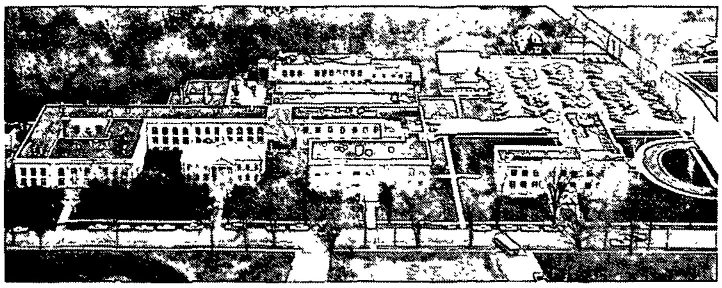

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SOLVENT PULPING — PROMISE AND PROBLEMS

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Solvent Pulping - Promise and Problems

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SOLVENT PULPING - PROMISE AND PROBLEMS

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In spite of renewed interest in solvent pulping, a conference devoted solely to this topic had not been contemplated until recently. That changed when Salman Aziz (IPC) and Mary Minton (Potlatch Corp.) suggested to Doshi & Associates that the time had come to bring together people from academia and industry for a technology update and a frank exchange of views. The conference was held June 16-17, 1987 in Appleton; a brief summary of papers and discussions is presented here.

Introductory remarks by Session Chairman S. Aziz included a brief review of organosolv pulping, from Kleinert's original concept to the present state of the technology. The alkaline processes produce stronger pulps than the acid catalyzed solvent systems, but recovery of alkali is an added complication. Magnesium salt catalysis may offer better properties and flexibility, as well as the possibility of pulping softwoods. Processes analogous to Kleinert's original uncatalyzed process are the most technologically developed. Nonsolvent technologies such as chemithermomechanical pulping (CTMP), and alkaline sulfite anthraquinone (ASAQ) pulping processes are active competitors in this area, while biopulping has yet to emerge as a viable alternative. During the discussion, questions centered around the merits of solvent pulping compared to conventional alternatives such as CTMP, etc., and the problems of solvent recovery and lignin usage in the former case.

Two hybrid processes at an advanced state of development are the Organocell and the Alkaline Sulfite Anthraquinone Methanol (ASAM) Processes. The former, developed in Germany, is at a demonstration stage using a continuous digester, with a bleached pulp capacity of 5 t/day. The process consists of hydrolyzing and softening the chips with ethanol-water at high temperature and extracting the lignin with caustic. Lignin is recovered as a powdery, low molecular weight material. Membrane technology and electrolysis are employed for caustic recovery. Pulps from softwoods approach the corresponding kraft pulps in strength. The project is funded in part by the German government.

The ASAM system is currently being developed by Patt and is in the process of being implemented on a pilot plant scale. The solvent system consists of alkaline sulfite and AQ in methanol. Patt claims this process produces pulps as strong as kraft with higher yields and significantly higher brightness. Bleaching a softwood ASAM pulp requires less than 3% chlorine in the C stage. It is possible to use a chlorine-free bleaching sequence to bleach softwood ASAM pulps to 90 brightness with strengths of kraft pulps. Here too, current research is directed at liquor recovery.

V. L. Chiang, from Michigan State University, described a response surface study of a methanol-sulfur dioxide pulping system for hardwoods. The parameters investigated were time, temperature, sulfur dioxide, and methanol content; and the responses were yield and kappa number. Future research will be directed toward optimizing pulping conditions for physical properties and bleachability.

R. A. Young and coworkers from the University of Wisconsin and T. Fredman of Biodyne Chemicals, Inc. reviewed ester pulping, the newest addition to the list of solvent pulping processes. Although a variety of acids and esters are available for this purpose, the acetic acid-ethyl acetate-water system was chosen for further study because it is believed to offer the possibility of simplified solvent recovery. The greater solubility (and reduced chemical modification) of lignin compared to other organosolv systems is also thought to be advantageous. It was claimed that capital expenditures for construction of an ester pulping unit would be considerably reduced and pollution problems would also be minimized compared to kraft.

Pulping trials demonstrated that pulps of very low lignin content and about 50% yield can be obtained from hardwoods, with strengths intermediate between kraft and sulfite pulps. Stronger reaction conditions were necessary for softwoods and the quality of the softwood pulps is not yet well established. Hard data describing the recovery process for both lignin and solvents and the applicability to softwoods would help make this process competitive with others.

Kyosti Sarkanen (University of Washington) described the difficulty of conducting kinetic analyses of acid catalyzed methanol pulping. He noted the usual sampling problems were compounded by the sensitivity of the process to seasonal growth variations and the presence of ash. Best results were obtained with ash-free chips and no more than 0.02<u>M</u> acid. The magnitude of the activation energy of the bulk delignification stage (80.3 kJ/mol) suggested that the rate determining reaction was the solvolytic cleavage of alpha-aryl ether bonds in the lignin matrix. The slower rate of lignin removal in a batch reactor compared to a flow-through reactor was thought due to the irreversible adsorption of dissolved lignin on fibers as a result of cooling during washing. It was concluded that a continuous acid-catalyzed process was desirable, that washing should be accomplished within the digester at elevated temperatures, and that objective pilot plant data are required before realistic comparisons can be made with conventional processes. Much discussion centered around the chemical nature of organosolv lignins, their isolation and their properties.

Helena Chum and coworkers (Solar Energy Research Institute) and Sarkanen described the use of organosolv pretreatments to prepare biomass materials for ethanol and lignin production. A statistical design showed acid catalysts favored xylan removal, while continuous flow conditions favored lignin removal. Longer times of reaction and lower pH also removed glucomannan and arabinoxylan. Lower methanol concentrations reduce the cost and the hazard involved in pulping. The resulting pulps were quite accessible to enzymes, since up to 46% of the wood was converted into fermentable sugars after enzyme hydrolysis. During the discussion, it was stated that the effectiveness of the enzymatic degradation is dependent upon the size of pores in the fibrous cellulosic substrate. While xylan removal facilitates accessibility by increasing pore size, its removal is often accompanied with loss of useful hexosans.

W. J. Bublitz reviewed his research dealing with full chemical pulping by mixtures of methanol and conventional sulfite liquors. Analysis showed that the use of 30% methanol represents an optimum for both yield and kappa number and a point of minimum shive content. Methanol should not be employed with bisulfite if rapid pulping is a goal. The addition of methanol slows delignification while it accelerates dissolution of lignin by solvent action. The rapid penetration of methanolic liquor into the wood chips reduces the possibility of burnt chip centers and makes isothermal sulfite cooking of many woods possible. The use of methanol in a pulp mill will require explosion-proof equipment as well as a good solvent recovery system. It was calculated that if 95% of the solvent is potentially recoverable, savings in wood costs can more than offset the cost of solvent make-up.

The ALCELL solvent pulping process (formerly known as the APR process) was described by J. H. Lora and associates from Repap Technologies Inc., who are planning to construct a 36 ton/day pulp mill to evaluate the commercial potential of the process. The ALCELL process is an alcohol based, noncatalyzed solvent technology which has already undergone 4 years of pulp testing, by-product investigation, and process development and considerable engineering and product feasibility analysis. Its advantages are that it can be built in small increments at relatively low capital cost to produce good quality hardwood pulp. It is claimed to be environmentally benign, lignin and saccharide can be isolated separately, and if markets can be found for these products, the ALCELL process promises to be unusually profitable. Its potential areas of application are to provide small increments of additional pulping capacity, to minimize pulp purchases, and to reduce environmental problems. It can also be of interest to developing countries limited by the size of their domestic market.

The key to the process is to sequence pulping in three stages, using displacement washing in the secondary and tertiary stages so that no further washing is required after the third stage. Since this can be accomplished on existing mill equipment, pilot plant development is proceeding rapidly.

Yields of aspen ALCELL pulps are comparable to the corresponding kraft pulps, while the versatility of the process makes it adaptable to most paper-making uses. Aspen pulp properties are intermediate between sulfite and kraft pulps. In general the pulps are more easily bleached than kraft. ALCELL lignin is ash free, has a low molecular weight, and is soluble in organics. The ensuing discussion centered around economic evaluation and recovery systems for by-products, reflecting the relatively advanced stage of this development.

The process is limited in its ability to delignify dense hardwoods or softwoods. Low lignin hardwood pulps (< 20 kappa and especially oaks) show a high degree of cellulose degradation. Cost analyses of the process need careful review with special attention to site specific conditions.

L. Pazner and P. H. Cho (University of British Columbia), described the use of alkali earth metal (AEM) salts as catalysts in high alcohol content cooking liquor for pulp production. The salt acts as a buffer and allows delignification of both hardwoods and softwoods to low kappa numbers without serious loss of pulp viscosity. The initially unsatisfactory strength properties and poorer flexibility of these pulps and fibers was caused by solvent dehydration of fibers. When rehydrated by dilute alkaline treatments and carefully refined, pulp strength properties compared favorably with kraft. The mechanism of AEM catalysis is not clearly known. Adsorption on wood followed by stabilization of acetyl groups is thought in some manner to minimize cellulose and hemicellulose degradation and prevent lignin polymerization.

An essential feature of the program was two panel discussions which aimed to get to the heart of some questions vital to the future of solvent pulping. In the first, chaired by Mary Minton (Potlatch Corp.), industry representatives were asked to articulate their needs, directing their remarks in particular to those in the audience actively engaged in research and development of organosolv processes. The latter group had its say in the second panel, chaired by Tom McDonough, when they responded to the first group's concerns.

The first panel began with an enumeration of the issues. These included the value of by-product lignin, minimum plant size, effects on the environment and the need for a simple and efficient recovery system. Emphasis was placed on the question of pulp quality, and the view was expressed that too much attention was being paid to tensile and tear. The niche for solvent pulping may lie in providing incremental pulp capacity for grades that do not have strength as their major requirement. To test the utility of a new pulp in tissue furnishes, for example, one should assess its potential for developing high water sorption capacity and rate, good softness and bulk, lack of self sizing tendency, and low yankee dryer adhesion. Similar lists of nonstrength-related properties can be identified for many other grades.

Bob Green (Mead Corp.), also downplayed the importance of strength, but for a different reason. Assuming that replacement of purchased hardwood kraft is contemplated, organosolv pulp produced on-site has a big advantage - it will never have to be dried. Hardwood pulps can lose as much as 50% in both tensile and tear upon drying. A potential disadvantage is that the slush pulp will be more difficult to dewater on the paper machine. To monitor this, the researchers should be measuring centrifugal water retention values.

Bill Nelson (Green Bay Packaging) spoke from another industrial viewpoint, that of a containerboard producer. He called for the development of more information on pulp properties vital to this sector of the industry. He is also concerned about the behavior of the pulp in existing refining, forming and drying systems; the capital invested in these areas is so large that replacement or extensive modification to handle a new furnish is out of the question. Questions concerning equipment performance are not easily answered without mill trials, which means that a pilot or demonstration unit capable of producing large quantities of pulp will be needed.

The other obstacles to industry acceptance of solvent pulping are, in Nelson's view, the confusing variety of systems being developed, many of them in a small way, and the lack of clear definition of process elements that will be needed for solvent containment. The implications of the latter point are complex and involve considerations of both workplace hazards and environmental impact. Insurance costs may be affected, and environmental authorities, when faced with such a new and unfamiliar process, will undoubtedly require extensive documentation and testing by the industry before permits are issued. A related concern is that when a permit is sought for a mill add-on providing incremental production, the entire mill may become subject to a new set of rules.

Nelson's final concern was sparked by the previous day's references to the species dependence of many of the processes described. Any process adopted by the industry will have to be free from this constraint. A wood furnish consisting of mixed species is the general rule and multiple single species lines are too expensive to be considered.

"Doug" Dugal (James River) expressed the opinion that comparisons with kraft are not appropriate; rather, one should identify, study and exploit special characteristics of solvent pulps to find appropriate applications for them, keeping in mind industry's need to develop new products. He further feels that we should take a lesson from the Brazilians' handling of the eucalyptus pulp development; take the risk of making the product first, then use its special properties to sell it.

The ensuing discussion from both the floor and the panel tended to corroborate the points made in the presentations (although there was some small amount of dissention), and brought out some additional points. Herb Hergert (Repap) stressed the importance of developing solvent pulping within the context of an integrated mill (as opposed to a market mill), and spoke out against viewing dissolving pulp as a "sink" for solvent pulps of inferior quality; quality requirements for dissolving pulps are more stringent than those for paper pulps. Kyosti Sarkanen, on the other hand, favored the concept of using organosolv pulping as part of an integrated rayon producing facility. The scale appears about right, and the operation of the pulping process could be tailored to the needs of the process.

The question of economics came out strongly during the discussion. One delegate related the results of an analysis of one of the leading solvent processes by his company: pulp quality is satisfactory, but the economic success of the process depends on a market for by-product lignin that does not exist. The lignin can be burned for energy, but then the economics become unattractive because of the capital cost of the boiler required. It was pointed out by another member of the audience, however, that organosolv lignin can be burned much more efficiently than kraft black liquor and the boiler requires correspondingly less capital investment.

When the discussion finally subsided, members of the second panel, representing the process developers, prepared to respond. Helena Chum led off, acknowledging that the efficiency of solvent recovery on a large scale remains an open question of considerable economic importance. In alcohol pulping, solvent costs at a recovery level of 94% would be higher than at 99% by \$60/ton

Referring to what he called a "chicken-and-egg" situation, Jairo Lora (Repap) reasserted the need to make pulp and lignin in large quantities to answer quality questions and facilitate market development. Repap is about to do just that in a 36 ton/day demonstration mill to be located in Canada's maritimes. He too downplayed the cost of reclaiming lignin's fuel value in the event that the market fails to materialize, and emphasized organosolv's advantages.

The panel discussions were rounded out by Kyosti Sarkanen's objective assessment. He characterized solvent pulping as a "new method of limited promise." Sarkanen believes that it may have a future in some integrated mill applications but not in market pulp. It will not be able to compete with chemimechanical pulping for communications grades but will fit well into an operation whose final product is rayon.

The ensuing discussion saw a variety of opinions vigorously expressed on, among other topics, R and D funding and the relationship of solvent pulping to chemimechanical and chemithermomechanical pulping. It was suggested that these chemimechanical methods may not be strong competitors for the solvent technologies as ways of adding incremental production. Very few of the existing CMP and CTMP installations can be viewed as such; they are greenfield operations or replacements for obsolete facilities. In addition, their development is hindered in many regions by their high energy requirements. On funding, the view was expressed that present difficulties in obtaining support from either industry or government would be alleviated by a concerted effort, such as the formation of a consortium to pursue well-defined objectives on an appreciable scale. It seems safe to conclude that what is needed here is leadership.

Details of the technical presentations are available in the form of a preprint book from Doshi and Associates, 2617 N. Summit St., Appleton, WI 54914.